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Stability of biodiesel and its blends: A review

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ABSTRACT

Biodiesel consists of long chain fatty acid esters derived from feed stocks such as vegetable oils, animal fats and used frying oil, etc. which may contain more or less unsaturated fatty acids which are prone to oxidation accelerated by exposure to air during storage and at high temperature may yield polymerized compounds. Auto oxidation of biodiesel can cause degradation of fuel quality by affecting the stability parameters. Biodiesel stability includes oxidation, storage and thermal stability. Oxidation instability can led to the formation of oxidation products like aldehydes, alcohols, shorter chain carboxylic acids, insolubles, gum and sediment in the biodiesel. Thermal instability is concerned with the increased rate of oxidation at higher temperature which in turn, increases the weight of oil and fat due to the formation of insolubles. Storage stability is the ability of liquid fuel to resist change in its physical and chemical characteristics brought about by its interaction with its environment and may be affected by interaction with contaminants, light, factors causing sediment formation, changes in color and other changes that reduce the clarity of the fuel. These fuel instabilities give rise to formation of undesirable substances in biodiesel and its blends beyond acceptable quantities as per specifications and when such fuel is used in engine, it impairs the engine performance due to fuel filter plugging, injector fouling, deposit formation in engine combustion chamber and various components of the fuel system.

The present review attempts to cover the different types of fuel stabilities, mechanism of occurrence and correlations/equations developed to investigate the impact of various stability parameters on the stability of the fuel. A review of the use of different types of natural and synthetic antioxidants has also been presented which indicates that natural antioxidants, being very sensitive to biodiesel production techniques and the distillation processes have varying impacts on fuel stability and available literature is very much scarce. The work on the use of synthetic antioxidants on the stability of biodiesel (both distilled and undistilled) from various resources has indicated that out of various 8 synthetic antioxidants studied so far only 3 antioxidants have been found to increase the fuel stability significantly. However, effectiveness of these antioxidants is in the order of TBHQ > PY > PG.

Contents

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Nomenclature

SVO	straight vegetable oil
ROOH	hydro peroxide
ASTM	American Society for Testing and Materials
UV	ultra voilet
RME	rapeseed methyl ester
IV	iodine value
AV	acid value
PV	peroxide value
ν	kinematic viscosity
PG	propyl gallate
BHA	butylated hydroxyanisole
BHT	butylated hydroxytoluene
TBHQ	tert-butyl hydroquinone
PY	Pyrogallol
CFPP	Cold filter plugging point
KOME	Karanja oil methyl ester
ME	methyl ester
OSI	Oxidation Stability Index
Cu	copper
Fe	iron
Ni	nickel
Sn	Tin
ppm	parts per million
TAN	total acid number
SME	soyabean methyl ester
FFA	free fatty acid
APE	allylic position equivalent
BAPE	bis-allylic position equivalent
IP	induction period
OX	oxidizability
O	oleic acid
L	linoleic acid
Ln	linolenic acid
FAME	fatty acid methyl ester
TME	tallow methyl ester
UFOME	used frying oil methyl ester

1. Introduction

Biodiesel is the monoalkyl ester obtained from the transesterification of agricultural lipids such as vegetable oil, animal fats, waste greases, waste cooking oil, etc. and has attracted renewed interest of researchers as substitute of diesel [1–128]. The fatty acid profile of biodiesel corresponds to that of parent oil or fat and is a major factor influencing its fuel properties. Due to the presence of significant amount of fatty acids with double bond, oxidative stability has been found to be of concern when the biodiesel is stored over an extended period of time. The storage problems can be caused by storage conditions like exposure to air and/or light, temperature as well as presence of metals with catalytic effect on oxidation. This fuel instability can give rise to sediments and gum formation and fuel darkening. The biodiesel and its blends have been found to be more prone to oxidation than the straight vegetable oils (SVO) and can develop wide variety of alcohols, aldehydes, peroxide, insoluble gum, sediments, etc. formed during its transport and long-term storage causing acidity in the fuel [1–4,26]. The use of such degraded biofuel in engine causes operational problems like fuel filter plugging, injector fouling, deposit formation in engine combustion chamber and in various components of the fuel system, thereby, affecting the engine performance badly [5,6]. Instability of fuel quality can be characterized by the indicators like formation of color, presence of soluble gums and insolubles in the fuel which are the important stability characteristics [6,7].

Overall stability includes oxidation, thermal and storage stability of biodiesel produced and its blends. Oxidation stability has been studied to establish relationship between induction period and other quality parameters [2,3,5,15,22,23,28,32,34,35,38,39,41–43,45–47,49,52–55,57,60,72,75,83,84,89,94,96,98,99,102,103,112,113,115,116,119–128]. Storage stability of a fuel is its ability to resist physical and chemical changes brought about by its action with environment and has been studied to investigate the effect of storage conditions on the stability of biodiesel/fuels [16–19,29,30,35,37,40,60,71,73,106,118, 120]. Thermal stability is concerned with the effect of temperature on the natural oxidation stability of the fuel and the effect of adding natural and synthetic antioxidants on fuel stability in order to improve fuel stability for longer period of time without any problems as referred to above [6–9,20,92,111]. A number of research papers have appeared on storage, thermal and oxidation stability of biodiesel from edible oils [1–109,111–123,125–128] but very little work is reported on the stability of biodiesel from non-edible oil resources like Jatropha curcas, pongamia, etc. [70,110,124]. The maintenance of biodiesel fuel quality depends on the development of technologies to increase its resistance to oxidation during long-term storage. Several approaches have been reported to be successful to increase the relative resistance to oxidation instability of fatty acid derivatives.

The paper attempts to review the work done on the oxidation, thermal and storage stability of biodiesel, mechanism of instability, correlations developed for all type of instability, etc.

2. Stability of biodiesel

Stability of biodiesel may be affected by intraction with contaminants, light, temperature, factors causing sediments formation, changes in color and other changes that reduce the cleanliness of the fuel [7]. Biodiesel produced from vegetable oils and other feed stocks have been found to be more susceptible to oxidation owing to the exposure to oxygen of the air and higher temperature, mainly, due to the presence of varying numbers of double bonds in the free fatty acid molecules. The chemical reactivity of fatty oils and their esters can, therefore, be divided into oxidative and thermal instability that can be determined by the amount and configuration of the olefinic unsaturation in the fatty acid chains. Most of the plant-derived fatty oils like soyabean and rapeseed contain poly-unsaturated fatty acids that are

methylene-interrupted rather than conjugated. This structural fact is key to the understanding both oxidative and thermal instability.

2.1. Oxidation stability

The oxidation of fatty acid chain is a complex process proceeded by a variety of mechanisms. Oxidation of biodiesel is due to the unsaturation in fatty acid chain and presence of double bonds in the molecule which offers high level of reactivity with O_2, especially, when it is placed in contact with air/water. The primary oxidation products of double bonds are unstable allylic hydroperoxides which are unstable and easily form a variety of secondary oxidation products. This includes the rearrangement of product of similar molecular weights to give short chain aldehydes, acids compounds and high molecular weight materials.

The work on the chemistry of oxidation reported by many researchers is based on the primary and secondary oxidation [8–24,114,117]. Some workers have proposed the vinyl polymerization mechanism in which higher molecular weight oligomers of fatty oils or esters can be formed [8,25]. The mechanism of oxidation is explained as follows:

2.1.1. Chemistry of oxidation

2.1.1.1. Primary oxidation. Peroxidation occurs by a set of reactions categorized as initiation, propagation, and termination [8] as in Fig. 1 which shows that first set involves the removal of hydrogen from a carbon atom to produce a carbon free radical. If diatomic oxygen is present, the subsequent reaction to form a peroxy radical becomes extremely fast even not to allow significant alternatives for the carbon-based free radical [9,10]. The peroxy free radical is not reactive compared to carbon free radical, but is sufficiently reactive to quickly abstract hydrogen from a carbon to form another carbon radical and a hydroperoxide (ROOH). The new carbon free radical can then react with diatomic oxygen to continue the propagation cycle. This chain reaction terminates when two free radicals react with each other to yield stable products.

During the initial period of oxidation, the ROOH concentration remains very low until a time interval, known as induction period, has elapsed that can be determined by the oxidation stability of the fatty oil or biodiesel under stressed conditions. Once the induction period is reached, the ROOH level increases rapidly indicating the onset of the overall oxidation process. Other properties of fatty oils and biodiesel fuels can also change directly or indirectly related to ROOH induction period in a similar way.

Fatty oils that contain more poly-unsaturation, are more prone to oxidation [8–24]. Literature reveals the relative rate of oxidation for the methyl esters of oleic (18:1), linoleic (18:2), and linolenic (18:3) acids to be 1:12:25 [11]. Further work has reported that the rate of oxidation of pure unsaturated fatty acids as measured by oxygen consumption in closed system is proportional to the number of bis-allylic carbons present [10,12]. As linoleic (18:2) and linolenic (18:3) acid content in fatty oils or esters increases, the

Initiation: $RH + I \rightarrow R\cdot + IH$

Propagation: $R\cdot + O_2 \rightarrow ROO\cdot$

$ROO\cdot + RH \rightarrow ROOH + R\cdot$

Termination: $R\cdot + R\cdot \rightarrow R\text{-}R$

$ROO\cdot + ROO\cdot \rightarrow$ Stable Products

Fig. 1. Primary oxidation reaction.

oxidation stability decreases and as fatty oils or the alkyl monoesters of fatty oils oxidize, the hydroperoxide (ROOH) levels also increase [13]. A number of studies have indicated that the development of ROOH over time exhibits one of the two behaviors: (i) ROOH levels can increase, achieve a plateau, and then be held at that level in a steady state and (ii) alternatively, ROOH levels can increase, achieve a peak level, and then decrease but no explanation is available on such behavior. However, the factors like oxygen availability, temperature, extent of pre-existing oxidation and the presence of metals that catalyzing the decomposition of hydroperoxides are likely involved in causing the primary oxidation [14,15,18–21].

2.1.1.2. Secondary oxidation. Once the fatty oil hydroperoxides are formed, they ultimately decompose to form aldehydes such as hexenals [22], heptenals, and propanal [13,23]. Hexanal, pentane, and 2,4-heptadienal have also been detected [23]. Increased acidity is always a result of oxidation of fatty oils and biodiesel leading to the formation of shorter chain fatty acids [14,16–18,24].

As hydroperoxides decompose, oxidative linking of fatty acid chains can occur to form species with higher molecular weights, i.e. oxidative polymerization. One of the obvious results of polymer formation is the increase in the oil viscosity [25]. Increased levels of poly-unsaturated fatty acid chains enhance the oxidative polymerization in fatty oils. During air oxidation at 250 °C, safflower oil high in linoleic (18:2) acid was found to have much more increase in viscosity than safflower oil high in oleic acid (18:1) [25]. The increase in viscosity is the direct indication of the presence of higher molecular weight materials in the oils.

As per European biodiesel standards EN 14213 and EN 14214, the oxidation stability measured by Rencimate apparatus has been found similar to the oil stability index (OSI) method [61]. Under the project stability of biodiesel (BIOSTAB), samples of ME from canola, sunflower oil, used frying oil and tallow were studied to determine which method shall be used to determine stability parameters [88]. In Europe, standard method EN 14112 referred to as Rencimate method was adopted as the standard method to determine oxidation stability and more recently, a method developed by Brazil as per resolution no. 42 of ANP has been considered as the most appropriate as the induction time, based on conductivity measurement of final product, displayed the best correlation with stages involved in the onset or preliminary oxidative degradation compared to American oil chemist society (AOCS) method (Cd 8-53) [17,42,62].

Since oxidation stability affects the fuel quality, this issue has been addressed in some standards and plans exist to include specification in other standards. Specification related to oxidation stability has been included in the European biodiesel standard EN 14214 and are intended for the American standards ASTM D6751.

FFA has been shown to have a significant effect on the oxidizability of the oil. Miyashita and Takagi [75] has compared the oxidation of oleic (18:1), linoleic (18:2) and linolenic (18:3) acids with their corresponding methyl esters and the free acids were each found to be far more unstable oxidatively than their corresponding ester. The trend of increasing stability for both acids and esters was found as linolenic < linoleic < oleic [75].

Table 1 shows the variation of induction period with fatty acid composition for methyl esters of different oils, collected from the literature. The graph of induction period vs % saturated fatty acids is shown in the following Fig. 2 which shows that the induction period increases as the % saturated fatty acids increases in the ME.

Fig. 3 shows the variation of induction period with % of unsaturated fatty acids. As indicated, the value of induction period increases as the % unsaturated fatty acids decreases in the ME.

Table 1
Fatty acid composition for different oils from various references.

S. no.	Type of ME	Saturated fatty acid	Unsaturated fatty acid	Induction period	Reference
1	CPOME	50.6	43.4	25.7	[99]
2	DPOME	48.73	51.27	3.52	[99]
3	UFOME	20.1	79.9	3.42	[60]
4	SBEME	41.4	58.6	14.59	[60]
5	POME	83.8	9.9	23.33	[60]
6	RU	9.69	90.32	9.1	[43]
7	RD	6.23	93.64	3.4	[43]
8	SU	11.7	87.92	3.4	[43]
9	SD	11.42	88.58	1.2	[43]
10	UU	20.25	77.6	5.9	[43]
11	UD	17.17	80.94	3.5	[43]
12	TU	41.11	55.76	1.2	[43]
13	TD	50.4	45.01	0.4	[43]
14	SOME	10.9	89.1	0.86	[103]
15	SOYABEAN ME	23.3	76.7	4.87	[98]
16	POME	83.8	9.9	15.4	[96]
17	ROME	64.5	29.7	7.8	[96]
18	JOME	21.1	78.9	3.23	[110]
19	POMNGAMIA ME	16	84	2.35	[110]
20	SOME	11.6	88.4	1.73	[110]
21	SOYABEAN ME	15.5	84.5	3.8	[110]
22	POME	43.4	56.6	13.37	[110]

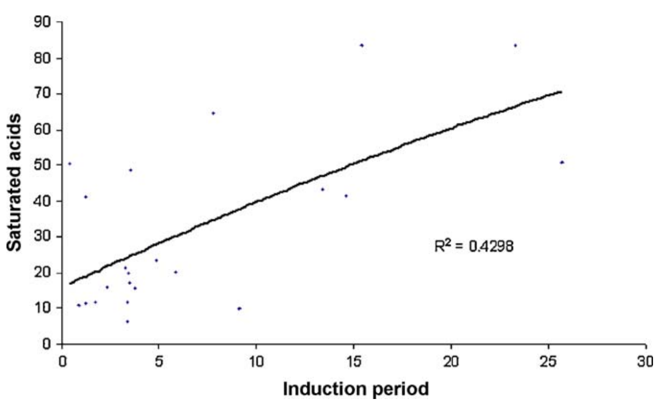


Fig. 2. Variation in induction period with % of saturated fatty acids in ME.

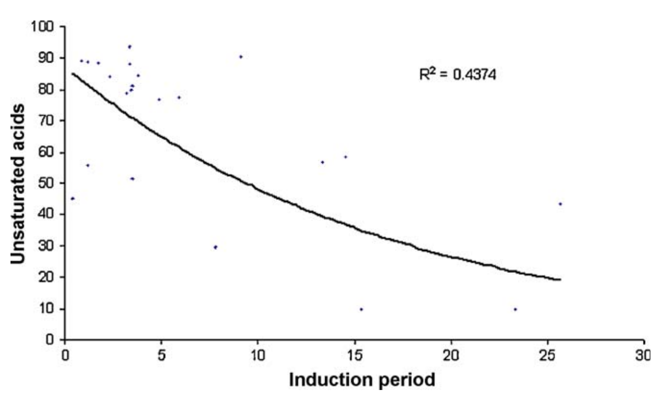


Fig. 3. Variation in induction period with % of unsaturated fatty acids in ME.

Though the value of R^2 in both the plots is found very less (0.4298 and 0.4374 respectively), which may be due to the presence of varying amount of methyl ester of different oils, depending on the technology of production including distillation of biodiesel, the natural antioxidants present in the raw materials are partially transferred to the corresponding esters in varying concentrations [95–97].

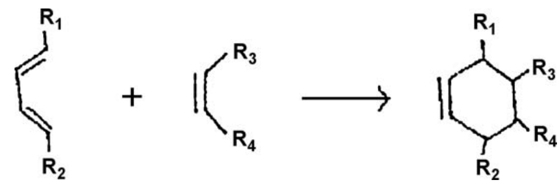


Fig. 4. Diels Alder reaction.

2.2. Thermal stability

Thermal oxidation is defined as the rate of oxidation reaction which increases weight of oil and fat due to its to exposure to high temperature (cooking temperature) conditions [6,7,20,89,92,111,120]. At sufficiently high temperatures, the methylene-interrupted poly-unsaturated olefin structure begins to isomerize to more stable conjugated structure. Once this isomerization has begun, a conjugated diene group from one fatty acid chain can react with a single olefin group from another fatty acid chain to form a cyclohexene ring [8,63,92]. This reaction between a conjugated di-olefin and a mono-olefin group is called the Diels Alder reaction, and becomes important at temperatures of 250–300 °C or more. The products formed are called dimmers [64,65,66]. The Diels Alder reaction is shown below in Fig. 4.

This reaction results in the formation of carbonyl compound such as aldehyde (formed from hydroperoxides) or high molecular weight polymers (formed from peroxide radicals) which increases the viscosity of biodiesel. Further it is found that there is quite a scarcity of literature available on the thermal stability of biodiesel. Dunn [7] has investigated the effect of temperature on the oil stability index (OSI) of biodiesel and reported that increasing the temperature accelerated the oxidation reaction, which decreased OSI of the FAME.

Many authors have reported on the effect of temperature on stability of biodiesel. Monyem et al. [20] investigated biodiesel thermal stability under simulated in-use conditions and reported that fuel temperature increases the oxidation process that gets accelerated and which results in increase in viscosity of fuel. Polavka et al. [53] studied temperature dependence of the oxidation induction period using Arrhenius equation. Hiroaki et al. [111] has evaluated the Thermal stability of biodiesel in supercritical methanol and it was found that poly-unsaturated fatty acid methyl esters such as methyl linoleate (18:2) and methyl linolenate (18:3) were extensively decomposed at 350 °C/43 MPa, accompanied by isomerization of *cis*-type double bonds into *trans*-type at 350 °C/43 MPa, whereas only methyl linolenate underwent a slight change in *cis*–*trans* isomerization at 270 °C/17 MPa without loosing the yield. Therefore, from these lines of evidence, it was concluded that the supercritical methanol treatment lower than 300 °C, preferably 270 °C with a pressure higher than 8.09 MPa, is appropriate to keep the maximal yield and thermal stabilization of biodiesel.

2.3. Storage stability

Storage stability is the ability of liquid fuel to resist change in its physical and chemical characteristics brought about by its interaction with its environment [69]. Customer acceptance, standardization and quality assurance are the key factors for introducing biodiesel and its blends into the market and storage stability is one such criteria. The stability of biodiesel during storage seems to be more severe than that for conventional diesel fuel. The resistance of biodiesel to oxidative degradation during storage is an important issue for the viability and sustainability of such alternative fuels.

Oxidation of unsaturated esters in biodiesel occurs by contact with atmospheric air and other pro-oxidizing conditions during long-term storage and impairs the fuel quality and subsequently affects the engine performance badly [69]. Storage stability may be affected by interaction with contaminants, light, factors causing sediment formation, changes in color and other changes that reduce the clarity of the fuel [7,68]. Several authors have performed long-term storage test on biodiesel quality and investigated the effect on the physical properties of the fuel with respect to time [18,69,70,71,124,126,127]. It was reported that viscosity, peroxide value, acid value and density of biodiesel increases but the heat of combustion decreases when stored for two years [18,69,70–72]. Viscosity and acid value (which can be strongly correlated), changed dramatically over one year with variation in Rancimat induction period depending on the feed stock but during 90-day storage tests, significant increases in viscosity, peroxide value, free fatty acid, anisidine value and UV absorption were observed [20,30,73]. Biodiesel from different sources stored for 170–200 days at 20–22 °C did not exceed viscosity and acid value specifications but induction time that decreased with exposure to light and air, has been found to have significant effect [16].

Bondioli et al. [19] and Thompson et al. [35] studied the deterioration of rapeseed oil methyl esters (RME) under different storage conditions including changes in acidity, peroxide value, and viscosity, and found that acid value (AV), peroxide value (PV) and viscosity (ν) increased with time [69]. Other authors [26] found a correlation between the oxidation stability and the amount of tocopherol as natural antioxidant. Bouaid et al. [69] studied the long-term storage stability of biodiesel from high oleic sunflower oil and used frying oil and showed that AV, density and viscosity decreased with increasing storage time while iodine value decreased. Further McCormick et al. [31] found that poly-unsaturated contents have the longest impact on biodiesel stability in terms of increasing insolubles formation and reduction in induction period.

The storage stability of poultry fat and diesel fuel mixtures studied by Geller et al. [71] was with respect to specific gravity, dynamic viscosity, sedimentation accumulation and separation (layering) including corrosive effects of the fuels on various metals. It was observed that viscosity and specific gravity of these biofuels changed very little over a storage period of one year. The addition of antioxidant up to 100% of the biofuel has been found to minimize the changes in physical properties and sedimentation over the course of the study. Energy was required to ensure proper mixing followed by homogenization for considerable time periods suggesting that mixing should only be performed immediately before the fuels are utilized. With regard to corrosive properties, brass and copper were found susceptible to attack by biofuels whereas 316 stainless steel and carbon steel were not.

Das et al. [124] have carried out long-term storage stability of biodiesel produced from Karanja oil and reported that the oxidative stability of Karanja oil ME (KOME) decreased, i.e. the peroxide value and viscosity increased with increase in storage time of the biodiesel. The samples stored under "open to air inside the room" and "exposed to metal and air" had high peroxide value and viscosity compared to other conditions, hence more susceptible to oxidative degradation. The effect of three antioxidants (PG, BHA and BHT) at varying loading was evaluated and found that oxidation stability of KOME increased with higher concentration of antioxidant levels. It was found that PrG is the best antioxidant for KOME followed by BHA and BHT.

Presence of certain metals such as Cu, Fe, Ni, Sn, and brass (a copper rich alloy) can increase the oxidizability of fatty oils [26]. Knothe and Dunn [26] indicated that presence of Cu, even in 70 ppm in rapeseed oil greatly increases the oxidizability of the fuel. Copper has also been found to reduce the Oxidation Stability Index (OSI) of methyl oleate more than either Fe or Ni. Bondioli et al. [18] has found that Fe is very effective hydroperoxide decomposer and its effect on rapeseed oil methyl esters was more pronounced at 40 °C than at 20 °C. Bessee et al. [74] indicated that Fe increases Total Acid Number (TAN) of soya methyl ester more than copper.

Sarin et al. [70] have studied the influence of metal contaminants on oxidation stability of Jatropha biodiesel and reported that even small concentrations of metal contaminants showed nearly the same influence on oxidation stability as large amounts. Copper showed the strongest detrimental and catalytic effect on the oxidation stability.

3. Measurement of stability

The fuel stability can be studied with respect to the following parameters.

3.1. Iodine value(IV)

This is one of the oldest and most common methods to determine the magnitude of unsaturation in fatty oil or ester [26,83,84]. D1541 and D1959 are the two available ASTM methods to measure IV though it is not necessarily a good method for assessing the stability as the stability depends on the position of the double bonds available for oxidation [12]. Knothe et al. also showed that OSI of various FAME correlates better with respect to BAPE equivalents than IV [26].

3.2. Peroxide value

Peroxide value is less suitable for monitoring oxidation as it tends to increase and then decrease upon further oxidation due to formation of secondary oxidation products [17,20,38]. When peroxide value reached a plateau of about 350 meq/kg ester during biodiesel (SME) oxidation, acid value and viscosity continued to increase monotonically [38]. Besides viscosity, acid value has a good potential as a parameter for monitoring biodiesel quality during storage [41].

3.3. Viscosity

Viscosity has been found to increase with chain length (number of carbon atoms) and with increasing degree of saturation. FFAs are responsible for higher viscosity than the corresponding methyl or ethyl esters. Double bond configuration influences the viscosity, i.e. *cis* double bond configuration giving a lower viscosity than *trans* while the position of the double bond affects viscosity to less extent [85]. Since oxidation processes lead to the formation of FFAs, isomerization of double bond usually *cis* to *trans* and formation of high MW products increases the viscosity with increasing oxidation. Based on the measurement of kinematic viscosities of 4 different biodiesel fuels and their blends with diesel, Yuan et al. [67] have found a viscosity–temperature relationship similar to that of diesel. Further a relationship between viscosity and specific gravity was also developed that can estimate viscosity from specific gravity of biodiesel. The accuracy of this method was found comparable to the weighted mass based semi log blending equation.

3.4. Structure indices

The allylic position equivalent (APE) is a theoretical measure of the number of singly allylic carbons present in the fatty oil or ester, assuming that all poly-olefinic unsaturation is methylene-inter-

Table 2
BAPE, APE, OSI and OX (oxidizability) for different ME.

S. no.	Type of ME	BAPE	APE	OSI	OX	Induction period	Reference
1	CPOME	9.48	86.4	3.4834	0.101598	25.7	[99]
2	DPOME	10.75	102.14	3.42625	0.115614	3.52	[99]
3	UFOME	34.4	155	2.362	0.35262	3.42	[60]
4	SBEME	13.2	113.2	3.316	0.14068	14.59	[60]
5	POME	10.2	19.8	3.451	0.102	23.33	[60]
6	RU	36.67	177.72	2.25985	0.378768	9.1	[43]
7	RD	36.85	182.3	2.25175	0.38094	3.4	[43]
8	SU	63.74	175.38	1.0417	0.64219	3.4	[43]
9	SD	61.18	177.16	1.1569	0.61728	1.2	[43]
10	UU	21.24	152.66	2.9542	0.223834	5.9	[43]
11	UD	23.68	158.94	2.8444	0.248408	3.5	[43]
12	TU	10.23	108.52	3.44965	0.111324	1.2	[43]
13	TD	5.87	85.8	3.64585	0.066222	0.4	[43]
14	SOME	74.8	178	0.544	0.7528	0.86	[103]
15	SOYABEAN ME	57.9	151.8	1.3045	0.58276	4.87	[98]
16	POME	10.2	19.8	3.451	0.102	15.4	[96]
17	ROME	39.1	59.4	2.1505	0.391	7.8	[96]
18	JOME	34.4	155	2.362	0.35262	3.23	[110]
19	POMNGAMIA ME	11.8	168	3.379	0.13244	2.35	[110]
20	SOME	61.8	163.2	1.129	0.62212	1.73	[110]
21	SOYABEAN ME	68.8	168.8	0.814	0.69268	3.8	[110]
22	POME					13.37	[110]

rupted. The bis-allylic position equivalent (BAPE) is a similar theoretical measure of the number of doubly allylic carbons present in the fatty oil or ester. Both APE and BAPE have been correlated with Oxidation Stability Index and peroxide value [26].

Knothe and Dunn [26] studied the influence of structure and concentration of individual fatty compounds on the oxidation stability of fatty acid esters. Other stability specifications like APE and BAPE for allylic and bis-allylic position equivalents takes into account both, the number and position of double bonds in the chains [86]. Knothe suggested APE and BAPE are better correlated to vegetable oils to observe properties [26].

Knothe has suggested the following relation to determine the APE and BAPE values [12]:

$$APE = 2 \times (A_{C18:1} + A_{C18:2} + A_{C18:3}) \quad (1)$$

$$BAPE = A_{C18:2} + 2 \times A_{C18:3} \quad (2)$$

where A is the amount of each fatty compound.

Table 2 reports the BAPE, APE, OSI and OX (oxidizability) as the stability parameters obtained by various researchers for different ME from different oil feed stocks.

APE and BAPE values were calculated for different oils ME using Eqs. (1) and (2) respectively defined by Knothe [12]. Figs. 5 and 6 show the variation of induction period with APE and BAPE value respectively. It is clear from the figure that as the APE and BAPE value decreases, the induction period increases indicating the credibility of the equations. But the value of R^2 is 0.43 and 0.22 for APE and BAPE respectively which is very less. The reason may be that amount of natural antioxidants is different in different oil ME depends upon the process of producing biodiesel and the process of distillation of biodiesel. The above results also indicate that impact of APE is more on induction period than that of BAPE.

Knothe [12] has also developed a correlation between OSI and BAPE as given below:

$$OSI = 3.91 - 0.045 \times BAPE \quad (R^2 = 0.983) \quad (3)$$

A plot of BAPE vs OSI calculated using Eq. (3) for different oil ME to check the credibility of the equation as shown in Fig. 7. The value of R^2 is 1 indicates that the relation is applicable to all the ME given in Table 2.

The relation between the OSI and induction period is shown in Fig. 8 in which the value of R^2 is very less (0.2172) indicates that the

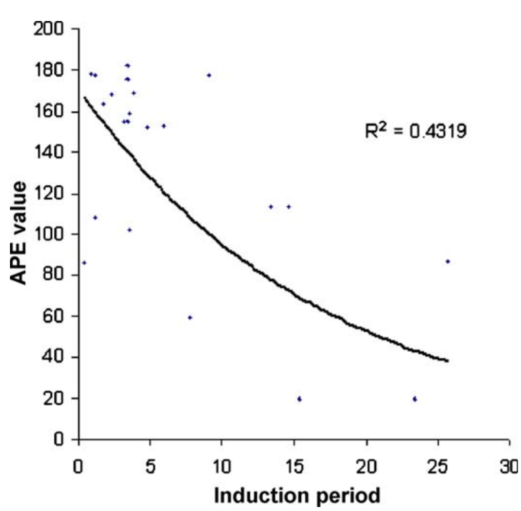


Fig. 5. Variation in induction period with APE value.

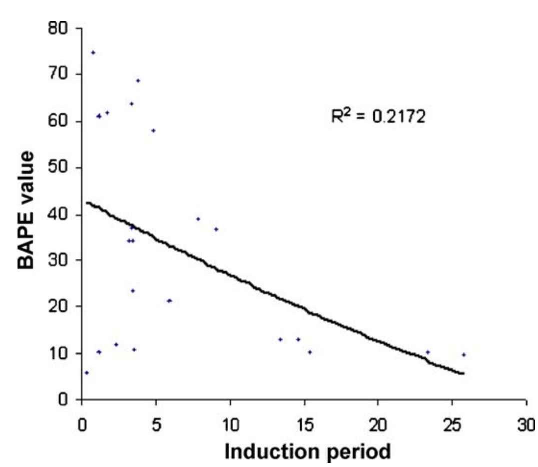


Fig. 6. Variation in induction period with BAPE value.

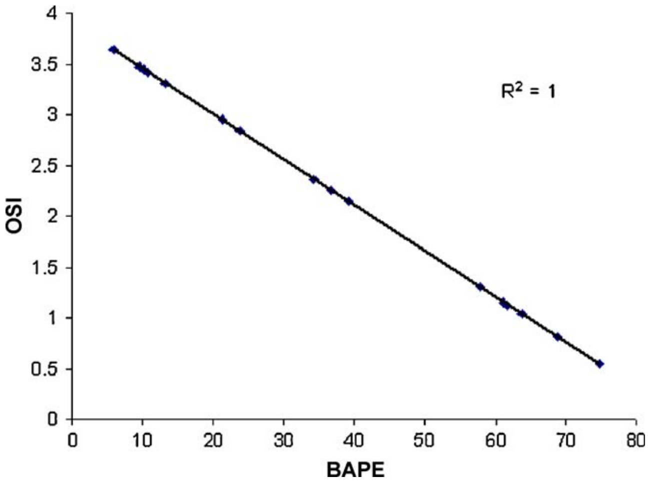


Fig. 7. Varation in OSI with BAPE value.

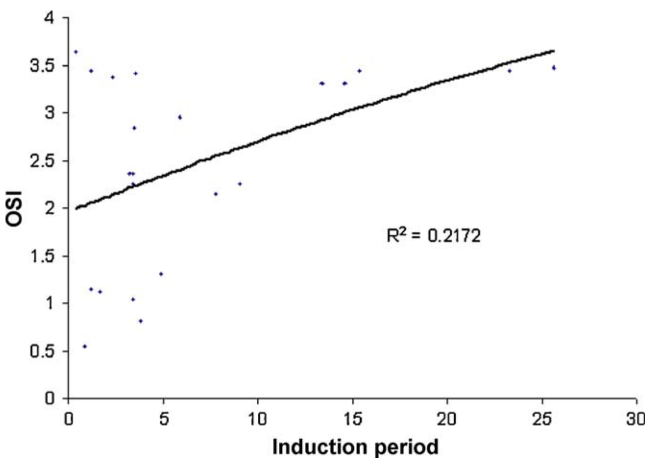


Fig. 8. Variation in induction period with OSI value.

relation is not applicable to all ME. The reason may be that the amount of natural antioxidants is different in different oil ME which depends upon the process of producing biodiesel and the process of distillation of biodiesel. Also same oil ME produced at different places may have different properties.

3.5. Oxidizability

Some authors have used another index of stability known as oxidizability (OX) as given by [87]:

$$OX = \frac{[0.02(\%O) + (\%L) + 2(\%Ln)]}{100} \quad (4)$$

where O refers to oleic acid (18:1), L refers to linoleic acid (18:2) and Ln refers to linolenic acid (18:3).

Fig. 9 shows the relation between oxidizability (OX) and induction period which indicates that OX decreases with increase in induction period and since the value of R^2 is very less (0.2255), therefore the relationship is not very reliable parameter.

4. Methods to increase the stability

Oxidation cannot be entirely prevented but can be significantly slowed down by the use of antioxidants which are chemicals that inhibit the oxidation process. Two types of antioxidants are generally known: chain breakers and hydroperoxide decomposers [94]. Literature related to hydroperoxide decomposers is very

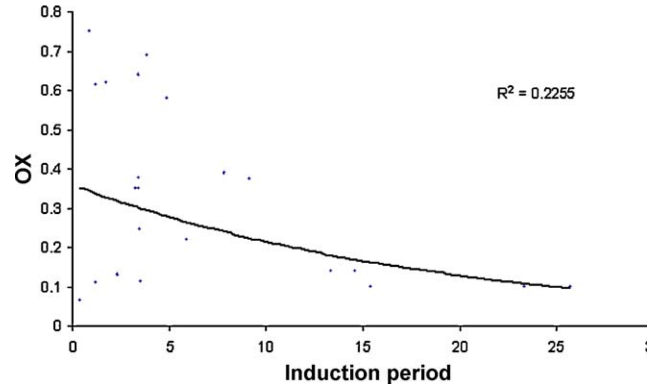


Fig. 9. Variation in induction period with OX.

$$ROO^{\cdot} + AH \rightarrow ROOH + A^{\cdot}$$

$$A^{\cdot} \rightarrow \text{stable product}$$

Fig. 10. Mechanism of all chain breaking antioxidants.

scarce. The two most common types of chain breaking antioxidants are phenolic and amine-types. Almost all the work related to stability of fatty oil and ester applications is limited to the phenolic type of antioxidant. The mechanism of all chain breaking antioxidants is shown below in Fig. 10.

As can be seen, the antioxidant contains a highly labile hydrogen that is more easily abstracted by a peroxy radical than fatty oil or ester hydrogen. The resulting antioxidant free radical is either stable or further reacts to form a stable molecule which is further resistant to chain oxidation process. Thus the chain breaking antioxidants interrupt the oxidation chain reaction in order to enhance stability.

The effectiveness of antioxidant is generally measured by stressing a fatty oil or ester molecule both with and without the antioxidant.

4.1. Sources of antioxidants

In fatty oils and esters, antioxidants can come from two sources: natural antioxidants (tocopherols) and synthetic antioxidants. Several studies are available showing the effect of antioxidants on the FAME stability [75–128].

4.2. Natural antioxidants

Tocopherol is a phenolic compound that exists in four isomers (α, β, γ, δ), all of which occur naturally in vegetable oils [76]. Depending on fatty oil processing conditions, tocopherols may be retained, partially lost, or completely lost [77,78]. Similarly, post-transesterification processing of biodiesel like distillation can remove any tocopherols that were originally present in the vegetable oil feed.

Unrefined vegetable oils containing natural antioxidants usually are found to have improved oxidative stability compared to the refined oils but do not meet other fuel specifications [29]. Natural antioxidants have also been deliberately added to biodiesel to investigate their antioxidant behavior.

Although numerous papers are available on the effect of natural and synthetic antioxidants on the stability of oils and fats little work is available on the effect of antioxidants on the behavior of FAME used as biodiesel. Mittelbach and Schober [43] studied the influence of a number of natural and synthetic antioxidants on the

oxidation stability of FAME from different feed stocks and reported that influence of the type and amount of antioxidants on undistilled and distilled biodiesel samples fulfill the requirements of current biodiesel specification.

Tahmasebi et al. [95] have reported the effects of various amounts of tocopherol extracted from maize flour [0.01%, 0.02%, 0.05%, 0.1%, and 0.2% (w/v)] on the oxidation of neat biodiesel (100% biodiesel). In this study the oxidation stability of biodiesel based on high oleic acid sunflower oil during the storage and distribution was studied using different percentages of maize flour [0.01%, 0.02%, 0.05%, 0.1%, and 0.2% (w/v)] contaminated by mycotoxins (useless for human consumption) as natural antioxidants. It was found that the antioxidant effect increased with concentration up to an optimal level, beyond which the increase in antioxidant effect with its concentration was relatively small.

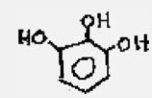
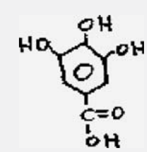
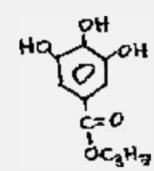
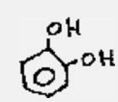
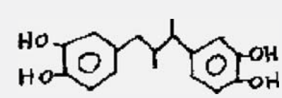
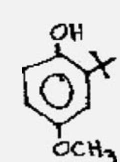
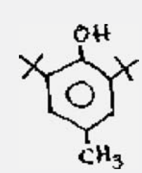
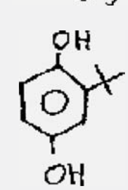
Fröhlich and Schober [96] studied the influence of tocopherols on the oxidation stability of methyl esters and found that the deactivation rates of tocopherols increased with unsaturation of the particular methyl ester and found the order of decreasing the effectiveness of natural antioxidants in ME as SME > R-RME > RVOME > TME. While α-tocopherol was found to be relatively weak, both β- and γ-tocopherols increased induction times significantly and may be added to methyl esters as natural antioxidants. Ito et al. [97] have optimized the tocopherol concentration in soybean oil deodorized distillate using response surface methodology.

4.3. Synthetic antioxidants

These antioxidants are added in oils or biodiesel to increase its stability. Some of the most common synthetic antioxidants are given in Table 3.

Different synthetic antioxidants had different effects on the stability of biodiesel, depending on the feed stock without affecting the properties such as viscosity, cold filter plugging point (CFPP), density, carbon residue and sulfated ash except acid value that appears to be affected slightly by the addition of antioxidants [43,47].

Table 3
Different synthetic antioxidants with their chemical formulae.

S. No.	Name of antioxidant	Abbreviation	Molecular formula
1	Pyrogallol	PY	
2	Gallic acid	GA	
3	Propyl gallate	PG	
4	Catechol	C	
5	Nordihydroguaiaretic acid	NDGA	
6	Butylated hydroxyanisole	BHA	
7	Butylated hydroxytoluene	BHT	
8	tert-Butyl hydroquinone	TBHQ	

Numerous studies have evaluated the effect of various synthetic antioxidants on the fatty oils and esters [21,41,43,47,52,60, 88,90,98–103,105–128]. A set of 28 phenolic antioxidants was evaluated with results ranging from 0 to 3.91. (Higher values imply better performance.) PY was the best, but GA, PG, and BHT also did well [108]. Evaluation of antioxidant effect of BHT, BHA, TBHQ, and PG on lard, various vegetable oils, and poultry fat [109] has indicated that in vegetable oils and poultry fat, TBHQ was the best performer. In lard, TBHQ was equivalent to BHA and better than the other two antioxidants.

Mittelbach and Schober [43] has further studied the influence of antioxidants on the oxidation stability of biodiesel and showed the influence of different synthetic and natural antioxidants on the oxidation stability using the specified test method. Biodiesel made from rapeseed oil, sunflower oil, used frying oil, and beef tallow (both undistilled and distilled) was used. The four synthetic antioxidants PY, PG, TBHQ, and BHA used were found to results in the greatest enhancement in the induction period. These four compounds and the widely used BHT were selected for further studies at concentrations from 100 to 1000 mg/kg. The induction periods of methyl esters from rapeseed oil, used frying oil and tallow were found to improve significantly with PY, PG, and TBHQ, whereas BHT was not very effective.

Schober and Mittelbach [47] have experimented the potential of 11 different synthetic phenolic antioxidants to improve the oxidation stability of biodiesel prepared from different feed stocks. Measurements of oxidation stability were carried out as per the European biodiesel specifications with a Rancimat instrument at 110 °C. At antioxidant concentrations of 1000 mg/kg, an improvement in oxidation stability could be achieved with all antioxidants tested. Especially the antioxidants di tert-butyl hydroquinone (DTBHQ), ionox 220, vulkanox zkf, Vulkanox bkf, and baynox were able to significantly improve the oxidation stability, leading to stabilization factors between 1.89 and 13.07. Variation of antioxidant concentrations between 100 and 1000 mg/kg showed that the efficiency of the antioxidants varied depending on the different types of biodiesel.

Dunn et al. [52] examined the effectiveness of five such antioxidants, tert-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PrG) and a-tocopherol in mixtures with soybean oil fatty acid methyl esters (SME) and found that increasing antioxidant loading (concentration) increases the activity also. Results showed that PrG, BHA and BHT were most effective and α-tocopherol least effective with respect to loadings up to 5000 ppm. Dunn [41] has further studied the effect of antioxidants on the oxidative stability of methyl soyate (biodiesel) and recommended BHA or TBHQ (loadings up to 3000 ppm) for safeguarding the auto oxidation of biodiesel during storage. BHT is also suitable at relatively low loadings (210 ppm after blending). PG showed some compatibility problems and may not be readily soluble in blends with larger SME ratios. Although α-tocopherol showed very good compatibility in blends but was significantly less effective than the synthetic antioxidants. Synthetic antioxidants, namely BHT and TBHQ are found to be more effective than natural antioxidant as agreed upon by with several research workers [60,100,101].

Domingos et al. [98] have experimented the influence of BHA, BHT and TBHQ in the oxidation stability of soyabean oil ethyl esters (biodiesel) and reported that BHT displayed the greatest efficacy in concentrations ranging from 200 to 7000 ppm. Other authors have reported that TBHQ displayed greater stability potential when used in higher concentrations and therefore is ideal for esters with lower stability [98,41].

Sendzikiene et al. [102] studied the oxidation stability of biodiesel produced from fatty wastes and suggested that the optimal level of synthetic antioxidants such as BHA and BHA for stabilization of fatty acid methyl esters was determined to be 400 ppm. Mixtures of methyl esters of animal and vegetable origin with antioxidants were more stable compared to pure products. The mixtures containing 80–90% of FAME of animal fat and 10–20% of FAME of vegetable oil with synthetic antioxidants were found to have highest oxidation stability.

The influences and the effectiveness of vitamin E, BHA, BHT, TBHQ and PG on the oxidative stability of UFOME were studied by Loh et al. [60] who found that PG gave the highest induction periods at higher concentrations (500–1000 ppm) followed by TBHQ, BHT, BHA, and vitamin E.

The kinetics of oxidation of biodiesel stabilized with antioxidant was studied by Xin et al. [103] who found that propyl gallate as antioxidant with concentration range from 250 to 5000 ppm at temperatures from 100 °C to 120 °C.

Many researchers have indicated that TBHQ was much more effective than the other additives demonstrating that both primary and secondary oxidation processes were inhibited under the conditions of the tests. The possible reason for TBHQ's superior performance was the fact that its immediate oxidation products still possessed antioxidant properties, unlike other commonly used synthetic antioxidants. In another study, TBHQ was found to reduce the amount of polymers formed during heating of olein at 180 °C [105]. It has been well established that BHT is among the best phenolic antioxidants for petroleum hydrocarbon materials such as fuels and lubricants while it was also found to be one of the least effective synthetic phenolic antioxidants in fatty oils and esters [52,88,104].

The BIOSTAB project evaluated 20 phenolic antioxidants at 1000 ppm and found PY and PG as the two best abbitives although TBHQ performed well [88]. The effect of commercially available antioxidants over biodiesel/diesel blends stability was studied by Dinkov et al. [106] who found both acidic and polymer products formed mainly contribute to the increase in density in untreated biodiesel/diesel blends and used three antioxidants for the purpose and found that addition of antioxidant butylated phenol to biodiesel/diesel blends led to reduction in insolubles formation including filterable, adherent and iso-octane insolubles.

Numerous studies have demonstrated that antioxidants are not always effective [88,90] and are, in fact, sometimes detrimental [21,88,90,107] to the stability of fatty oils and esters.

Sarin et al. [110] have experimented on Jatropha biodiesel and found an optimum mix for Asia using different blends of biodiesel from palm and Jatropha oil for improved oxidation stability. Jatropha biodiesel, when blended with palm methyl ester, leads to good oxidation stability. The stability of biodiesel is very critical and biodiesel requires antioxidant to meet storage requirements and to ensure fuel quality at all points along the distribution chain. In order to meet EN 14,112 specification, around 200 ppm concentration of antioxidant is required for biodiesel (except palm biodiesel) which is much higher than that required for petroleum diesel. To minimize the dosage of antioxidant, appropriate blends of Jatropha and palm biodiesel were made and it was found that antioxidant dosage could be reduced by 80–90%, if Palm oil biodiesel is blended with Jatropha biodiesel at around 20–40% concentration. Since palm biodiesel has poor low temperature properties like cloud point and pour point, the blending of Jatropha biodiesel improves the same.

Liang et al. [99] have examined the effect of natural and synthetic antioxidants on the oxidative stability of palm diesel and found that CPOME containing not less than 600 ppm of vitamin E were found to exhibit oxidative stability of more than 6 h and thus, conform to the specification of the European standard for biodiesel (EN 14,214). While DPOME needs to be treated with antioxidants in order to meet the specification. Synthetic antioxidants, namely BHT and TBHQ are found to be more effective than natural

Table 4
Results of the use of antioxidants for oxidation stability of different oil ME.

S. no.	ME used	Result	Concentration of antioxidants (ppm)	Reference no.
1	Rapeseed oil ME (undistilled)	TBHQ > PG > PY > BHA > BHT	1000	[43]
2	Rapeseed oil ME (distilled)	PY > PG > BHA > TBHQ > BHT	1000	[43]
3	Used frying oil ME (undistilled)	PY > PG > TBHQ > BHA > BHT	1000	[43]
4	Used frying oil ME (distilled)	PY > PG > TBHQ > BHA > BHT	1000	[43]
5	Sunflower oil ME (undistilled)	PY > PG > TBHQ > BHA > BHT	1000	[43]
6	Sunflower oil ME (distilled)	TBHQ > PG > BHA > PY > BHT	1000	[43]
7	Tallow MEB (undistilled)	PY > TBHQ > PG > BHA > BHT	1000	[43]
8	Tallow ME (distilled)	PG > PY > TBHQ > BHT > BHA	1000	[43]
9	Rapeseed oil ME	Baynox	–	[47]
10	Recycled cooking oil ME	DBHQ	–	[47]
11	Distilled recycled cooking oil ME	Vulkanox BKF	–	[47]
12	Tallow ME	10 NO_x 220	–	[47]
13	Methyl soyate	BHA ~ PrG > TBHQ ~ BHT > α-tocopherol	2000	[52]
14	Used palm oil ME	PG > BHA > TBHQ > BHT > vitamin E	1000	[60]
15	Soyabean ME	γ-Tocopherol > δ-tocopherol > α-tocopherol	1000	[96]
16	Tallow ME	δ-Tocopherol > γ-tocopherol > α-tocopherol	1000	[96]
17	Soyabean oil ethyl ester	BHT > BHA > TBHQ	1000	[98]
18	Soyabean oil ethyl ester	TBHQ > BHT > BHA	7000	[98]
19	PALM DIESEL	TBHQ > BHT > α-tocopherol	1000	[99]
20	Palm olein	TBHQ > PG > THBP > BHT > DLTDP > BHA	–	[100]
21	Refined palm oil	TBHQ > BHT > BHA	200	[101]
22	Tallow ME	BHT > BHA	400	[102]
23	Rapeseed ME	BHA ~ BHT	400	[102]

antioxidant. The efficiency of antioxidants investigated in the study was as follows: TBHQ > BHT > α-tocopherol.

Augustin and Berry [100] determined the effectiveness of antioxidants in refined, bleached and deodorized palm olein and found that The addition of antioxidants BHT, PG and TBHQ, at a level of 200 ppm to refined, bleached and deodorized (RBD) palm olein resulted in the retardation of the oxidative deterioration of the oil when stored at 60 °C for a period of 10 weeks. BHA proved to be a relatively ineffective antioxidant, whereas TBHQ afforded the most protection for the RBD olein.

Fritsch et al. [101] have examined the effect of antioxidants on refined palm oil and found TBHQ to have better effect as antioxidant on refined palm oil than BHT and BHA. Sharma et al. [127] worked on low temperature properties of biofuel and their blends with petroleum diesel and found that that biofuels produced by either pyrolysis or transesterification can be used at levels up to 10% by weight in fossil fuels without significantly affecting the low temperature properties, oxidation stability and corrosion properties and thus demonstrate significant potential as biofuels. Araújo et al. [128] have evaluated the oxidation stability of castor oil FAME using 4 different types of antioxidants. The results indicate different performances of the antioxidants as well as synergisms between antioxidants and biodiesel. In general, the addition of antioxidants increased from 6 to 15 times the stability of castor oil FAME with BHA showing the best results for improving antioxidation in castor oil biodiesel.

Table 4 shows the relative effectiveness of synthetic antioxidants on the oxidation degradation of biodiesel.

Table 4 shows the most effective synthetic antioxidant is TBHQ followed by PY and PG. however BHA and BHT are found to be less effective as reported in the literature. It is also apparent from the table that natural antioxidants such as different tocopherols and vitamin E are significantly less effective than synthetic antioxidants.

Based on the above literature review it is found that much work has been done on the mechanism of degradation of oils and fats. It is observed that instability behavior is due to degree of unsaturation in oils. Various stability related parameters have also been developed by different researchers (OSI, IP, PV, BAPE, APE, etc.) but no perfect correlation has been found between them. Also various methodologies have been developed by various researchers to increase the stability of biodiesel. However there is scope to do work for biodiesel from non-edible sources.

5. Conclusion

The acceptance of biodiesel quality by the markets and consumers is of considerable significance. The biodiesel stability may be affected by large number of parameters which can be categorized by oxidation, thermal and storage stability parameters. The present review has covered the different types of the fuel stabilities, mechanism of occurrence and correlations/equations developed to investigate the impact of various stability parameters on the stability of the fuel. Main parameters related to stability are PV, AV, IP, BAPE, APE, OSI and OX. Various correlations have been developed between these parameters, collected from literature, to check the effect of these parameters on the stability of biodiesel. The relation between IP and %saturated acids as well as %unsaturated acid is found to be good with value of R^2 being 0.4298 and 0.4374, respectively. Relationship between induction period with APE and BAPE has also been investigated and it was found that impact of APE is more on induction period than with that of BAPE.

A review of the use of different types of natural and synthetic antioxidants has also been presented which indicates that natural antioxidants, being very sensitive to biodiesel production techniques and the distillation processes have varying impacts on the fuel stability. The work on the use of synthetic antioxidants on the stability of biodiesel from various resources have indicated that out of various synthetic antioxidants studied so far only 3 antioxidants have been found to increase the fuel stability significantly. However, effectiveness of these antioxidants is if the order of TBHQ > PY > PG. The review reveals that, lot of work is required to be done for stability of non-edible oils. Apart from this, additional research is required to be done to investigate the effect of stability of biodiesel on engine performance as well as effect on emissions.

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